

This Page Is Inserted by IFW Operations  
and is not a part of the Official Record

## **BEST AVAILABLE IMAGES**

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images may include (but are not limited to):

- BLACK BORDERS
- TEXT CUT OFF AT TOP, BOTTOM OR SIDES
- FADED TEXT
- ILLEGIBLE TEXT
- SKEWED/SLANTED IMAGES
- COLORED PHOTOS
- BLACK OR VERY BLACK AND WHITE DARK PHOTOS
- GRAY SCALE DOCUMENTS

**IMAGES ARE BEST AVAILABLE COPY.**

**As rescanning documents *will not* correct images,  
please do not report the images to the  
Image Problem Mailbox.**

## The Structure of Evaporated Metal Films and Their Optical Properties

R. S. SENNETT\* AND G. D. SCOTT

Department of Physics, University of Toronto, Toronto, Canada

(Received January 6, 1950)

The structure of evaporated films of eight different metals in thicknesses from 30 to 800 Å has been observed in the electron microscope and correlated with their optical properties. The stable form of films thinner than a characteristic thickness was found to be aggregated. For each film the absorptions for wavelengths in the visible were determined from the measured transmissions and reflections. The rate of evaporation is shown to affect the structure and the optical properties, slow rates in general giving more aggregated structure and increased light absorption.

The Garnett theory has been used to explain the peculiar variation with thickness of the optical properties of thin metallic films in terms of the observed structure of the films and the bulk properties of the metal. The presence or absence of absorption maxima and their change with wave-length can be predicted qualitatively on the basis of this theory for all the films studied.

### INTRODUCTION

It is well known that thin films of a number of metals show brilliant colors while those of other metals have only a metallic appearance. The similarity between the colors of gold films and colloids of that metal was first reported by Faraday<sup>1</sup> in 1857 and led him to suggest an aggregated structure for the thin films.

The optical constants,  $n$  the refractive index and  $k$  the extinction coefficient, have been determined for metallic films by a number of different methods. Pogany<sup>2</sup> found  $n$  and  $k$  for platinum, palladium, gold, and silver films from the change in polarization of light reflected from the films. However, most workers have measured the transmission and reflection of the films and employed graphical methods<sup>3</sup> to determine the values of  $n$  and  $k$ . In this way Murmann<sup>4</sup> found a maximum in the product  $nk$  for silver films at a thickness of approximately 100 Å. Krautkrömer has reported a similar variation in the case of gold films.<sup>5</sup>

The electromagnetic theory was applied to the optical properties of thin films by Drude<sup>6</sup> in 1894. This gave good agreement with experiment for films thicker than about 200 Å by assuming that the films were continuous. However to maintain the agreement in thinner films a marked change of the optical constants with thickness had to be postulated. In 1904 Garnett<sup>7</sup> showed that this change in the optical constants from those of the bulk metal could be explained by assuming that the thinner films were composed of numerous small aggregates.

In the early work the structure of films could be inferred only from studies of the various properties. Light microscope observations showed that in thick

films of a number of metals aggregates appeared upon heating.<sup>8</sup> Though x-ray and electron diffraction studies<sup>9</sup> suggested that metal films in general are aggregated, this fact has been proved conclusively by electron microscope observations.<sup>10,11</sup> These latter results have shown that films of most metals thinner than a characteristic thickness are composed of separate aggregates with definite channels between them. However no detailed comparison has been reported between the structure observed in the electron microscope and the experimentally determined properties.

### EXPERIMENTAL

The variation with thickness of the structure and of the optical properties was determined for films of the following metals: silver, gold, copper, aluminium, antimony, nickel, palladium, and chromium.

The films were formed by vacuum evaporation of the metal from a tungsten filament or a molybdenum boat. The techniques involved in such evaporations have been

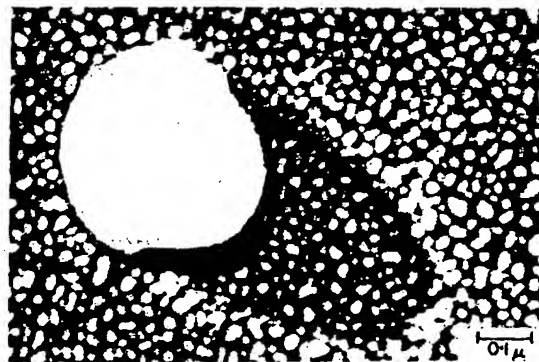


Fig. 1. Similarity of the structure of silver on Formvar and on silica substrates.

\* Part of this research was carried out while one of the authors (R.S.S.) was a holder of a Studentship from the National Research Council of Canada.

<sup>1</sup> M. Faraday, *Trans. Roy. Soc. (London)* 147, 145 (1857).

<sup>2</sup> B. Pogany, *Ann. d. Physik* 49, 531 (1916).

<sup>3</sup> K. Försterling, *Ann. d. Physik* 30, 745 (1937).

<sup>4</sup> H. Murmann, *Zeits. f. Physik* 80, 161 (1933).

<sup>5</sup> J. Krautkrömer, *Ann. d. Physik* 32, 537 (1938).

<sup>6</sup> P. Drude, *Ann. d. Physik* 51, 77 (1894).

<sup>7</sup> J. C. M. Garnett, *Trans. Roy. Soc. (London)* 203A, 385 (1904).

<sup>8</sup> E. N. da C. Andrade and J. G. Martindale, *Trans. Roy. Soc. (London)* 235A, 69 (1935).

<sup>9</sup> A. G. Quarrell, *Proc. Phys. Soc. (London)* 49, 279 (1937).

<sup>10</sup> R. G. Picard and C. S. Duffendack, *J. App. Phys.* 14, 291 (1943).

<sup>11</sup> H. Levinstein, *J. App. Phys.* 20, 306 (1949).

## Structure and Optical Properties of Silver Films Rapidly Evaporated (2 Seconds)

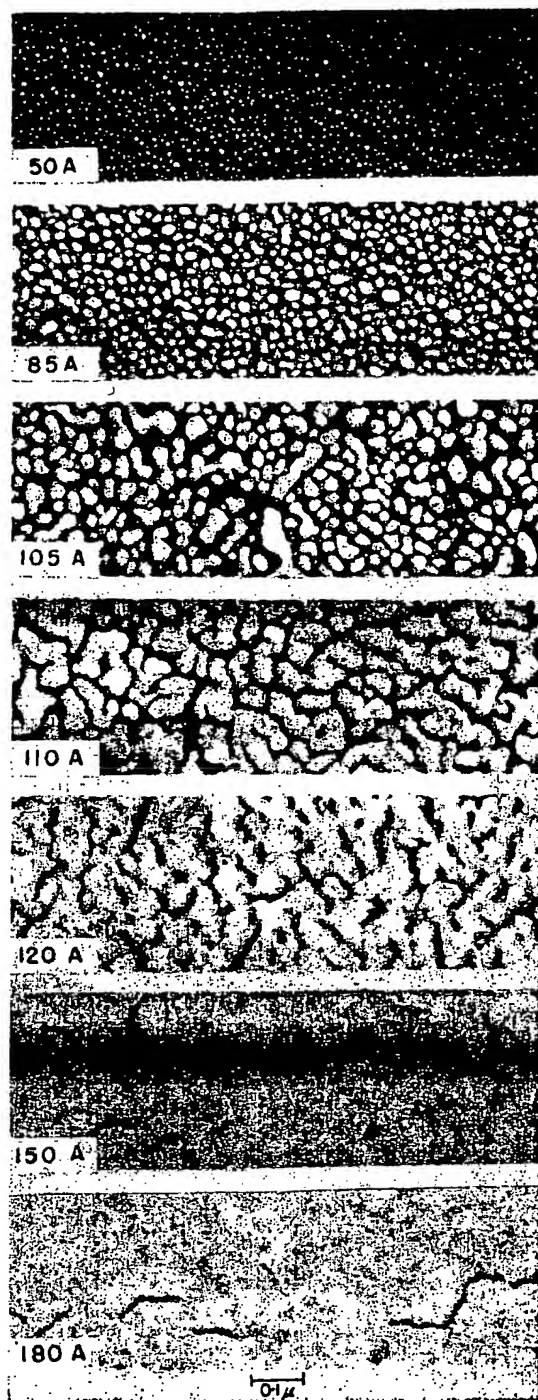


FIG. 2a. Electron micrographs of silver films showing the structure at the seven indicated thicknesses.

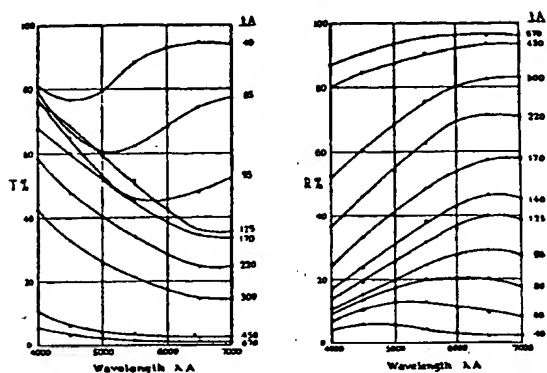


FIG. 2b. Wave-length variation of the transmission and reflection of silver films for different thicknesses.

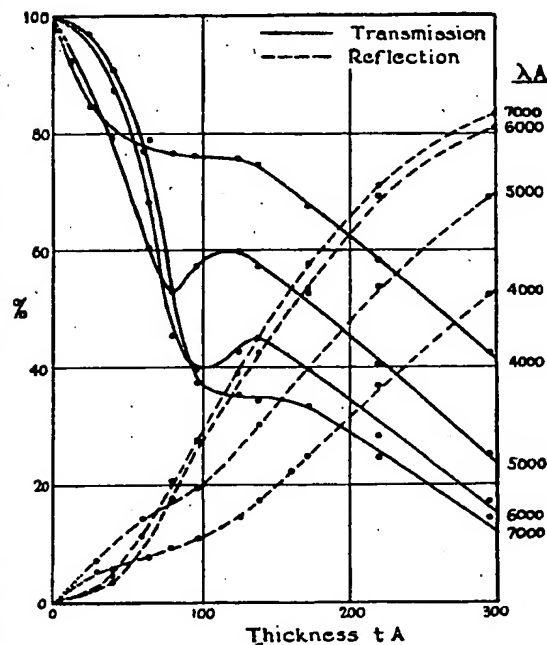


FIG. 2c. Variation of transmission and reflection with thickness.

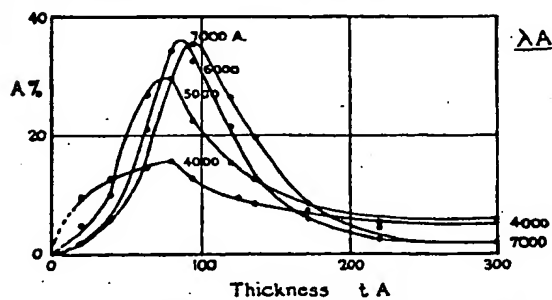


FIG. 2d. The absorption of silver films against thickness for different wave-lengths.

## Structure and Optical Properties of Silver Films Evaporated Slowly

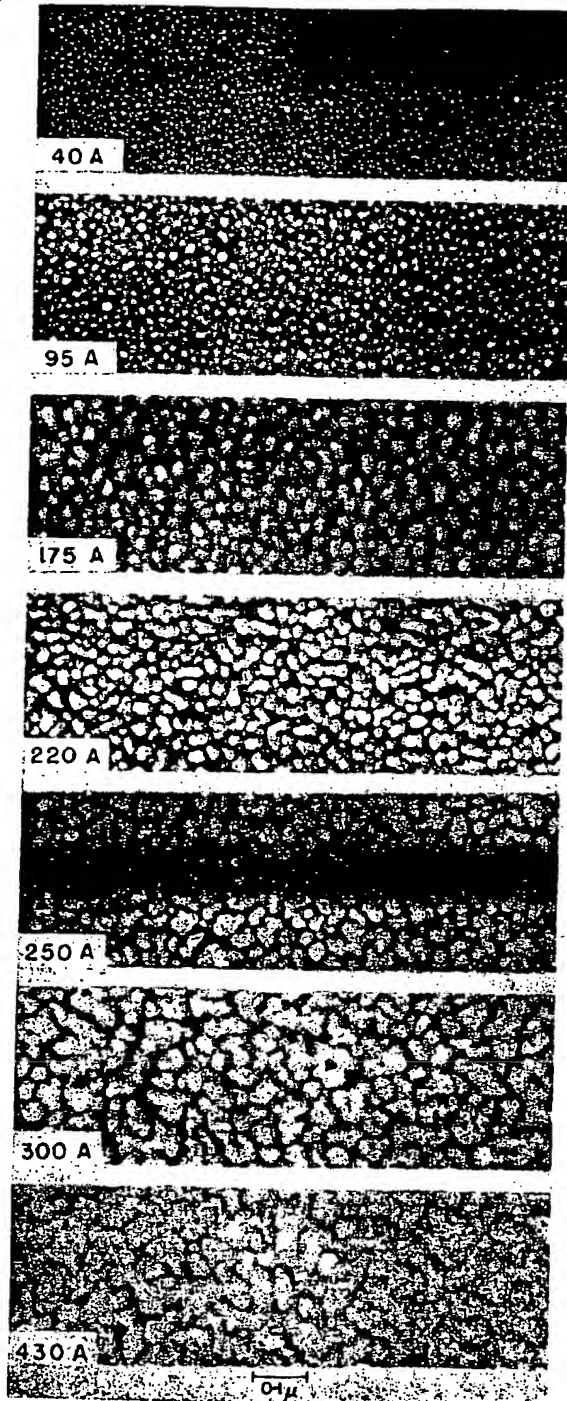


FIG. 3a. Electron micrographs of silver films deposited in 20 minutes.

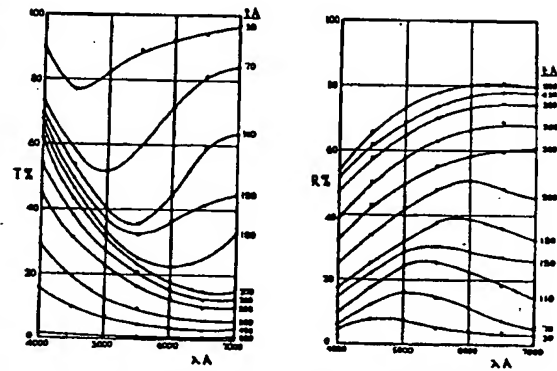


FIG. 3b. Transmission and reflection of silver films deposited in 20 minutes.

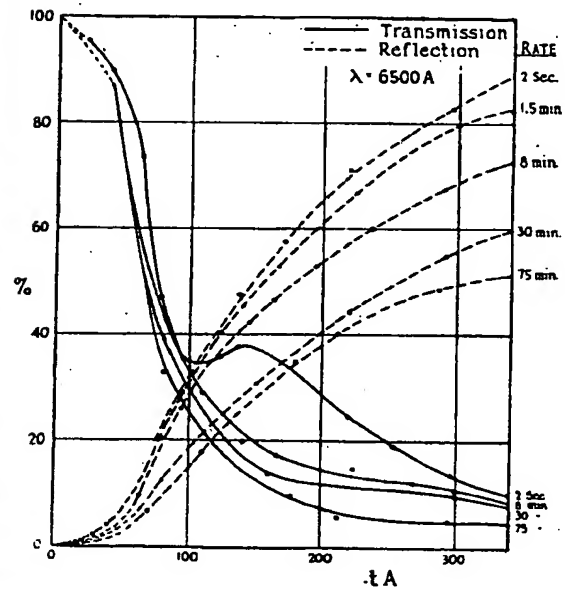


FIG. 3c. Variation of transmission and reflection with thickness for different times of evaporation (at 6500 Å).

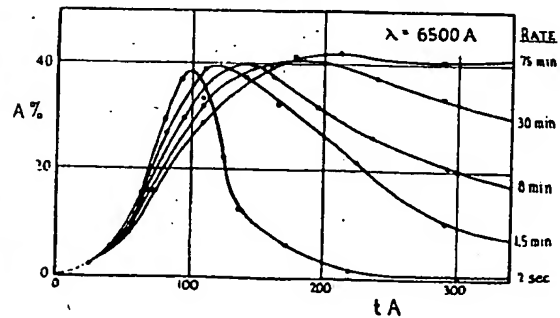


FIG. 3d. The absorption of silver films against thickness for different rates.

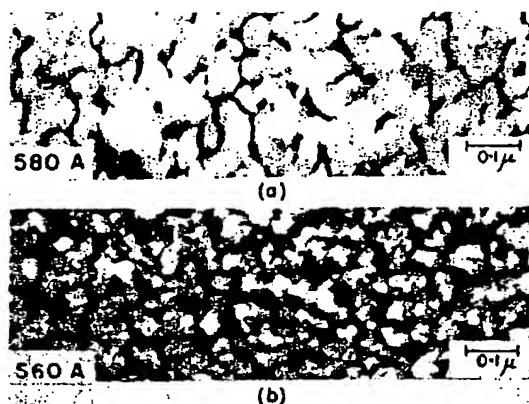


FIG. 4. Difference in structure of silver films of approximately the same thickness (a) deposited in 20 min. (b) deposited in 75 min.

outlined by Olsen, Crittenden, and Smith.<sup>12</sup> The pressure in the evaporating unit was in all cases below  $10^{-4}$  mm Hg. It was found that, for a given thickness, films produced even at quite large angles of incidence of the metal on the substrate were similar in structure and optical properties to those produced at normal incidence. For this reason a range of thicknesses was obtained from each evaporation by using the variation with both distance and angle of incidence along a plane surface. One or two 3-in. microscope slides usually provided an adequate series of thicknesses.

Mounts for examination of the films in the electron microscope were made on Formvar film about 150Å thick, supported by stainless steel mesh, which were placed along the microscope slide. The mounts were of necessity exposed to the atmosphere for a short time (up to 30 min.) before being transferred to the microscope, but for the metals studied apparently no change in structure occurred. This has been verified by a comparison of the structure of films formed by evaporation within the microscope, a report on which is to be presented elsewhere. Electron diffraction of silver films exposed to the air for several days indicated the presence of silver sulphide and silver oxide, but no trace of these impurities could be found in samples exposed up to thirty minutes.

In obtaining micrographs care was taken to prevent possible effects of the electron beam such as elevated local temperatures and contamination which are known to occur with high intensity and long exposures. Though it has been suggested that the aggregated structure observed in many thin metallic films may be due to bombardment by the electron beam,<sup>13</sup> it was demonstrated that this was not so by shadow-casting an aggregated film before placing it in the microscope. The image in this case showed each aggregate with its

corresponding shadow proving that the aggregates were unchanged from those in the original film.

The optical transmissions and reflections of the films were determined using a constant deviation spectroscoposcope fitted with a photo-multiplier 931A. The glass microscope slide with the film was mounted on the table of a goniometer which carried a white-light source, a condensing lens and a lens to project an image of a small area of the film onto the slit of the spectroscoposcope. Both the source and the power supply for the photo-multiplier were stabilized. With the output of the photomultiplier connected directly to a microammeter, the response of the system was linear with incident intensity for output currents up to 250 microamp. The transmissions and reflections of film areas  $2 \times 0.5$  mm could be determined to  $\pm 2$  percent for wavelength bands of less than 100Å throughout the visible.

The transmission coefficient,  $T$ , of the film was determined by taking the light transmitted by the clear glass as reference intensity. For the reflection coefficient,  $R$ , the reflection from a previously measured silver surface was used as reference intensity. An approximate correction to  $R$  was made by subtracting  $T^2 R_0$  from the observed reflection for the film on the slide, where  $R_0$  is the reflection of the glass slide itself. The absorption coefficient of the film,  $A$ , was found by assuming  $T + R + A = 100$  percent. It is clear that  $A$  includes the light scattered by the film. The scattered light was measured at different angles for a slowly evaporated silver film 150Å thick and it was estimated that the total scattering was about 1.5 percent at 5500Å. The value of  $A$  in this case was about 40 percent. Since for smaller absorptions it was found that the scattering was even a smaller fraction of  $A$ , it was considered that for the purposes of this paper the scattering could in all cases be neglected.

It is to be noted that the optical properties were measured for films deposited on glass whereas the structure was observed for films on Formvar. It was found however that films produced on Formvar coated glass slides had the same optical properties as films similarly produced on glass itself. Furthermore the structure of a film on Formvar was found to be the same as that of the film on silica. This is illustrated in Fig. 1, which is a micrograph of an aggregated silver film. Polystyrene spheres<sup>14</sup> on Formvar were first heavily shadow-cast with silica before evaporating the silver, so that in the



FIG. 5. Gold film 75Å thick, deposited in 2 sec.

<sup>12</sup> Olsen, Crittenden, and Smith, *J. App. Phys.* 16, 425 (1945).

<sup>13</sup> D. A. Was, *Physica* 6, 382 (1939).

<sup>14</sup> R. C. Backus and R. C. Williams, *J. App. Phys.* 20, 224 (1949).

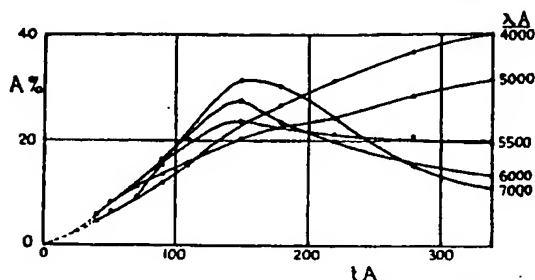


FIG. 6. The optical absorption of (2-sec.) gold films against thickness for different wave-lengths.

"shadow" the silver has a Formvar substrate whereas in the adjacent areas it has a silica substrate. It is evident that the aggregated structure is similar in the two areas.† Similar observations were made for Formvar and chromium as substrates for silver. For certain metals, e.g. zinc and cadmium (not among those considered here), the structure on chromium was found to be different from that on Formvar.

The thicknesses of the films could be estimated from the mass of metal evaporated. However measurements, which were accurate within 5 percent, were made by an extension of the multiple interference method discussed by Tolansky.<sup>13</sup> This yields an *average* value equivalent to that given by the mass per unit area for aggregated as well as continuous films. Details of the techniques employed here will be published separately.

## RESULTS

### (a) Silver

The major part of the experimental work was done with silver films which, with decreasing thickness, display blue and red colors. A series of micrographs indicating the change in structure with thickness for rapidly evaporated silver films is given in Fig. 2a. The micrographs indicate that as the film grows the aggregates initially formed increase in size but at first remain well separated. With increasing thickness the aggregates begin to join and then merge together leaving only a few "cracks" which in turn are finally obliterated.

The transmissions and reflections of these films are plotted against wave-length in Fig. 2b and against thickness in Fig. 2c. The absorptions have a maximum for all wave-lengths at thicknesses somewhat less than 100Å (Fig. 2d). As can be seen from the micrographs this is just below the "critical" thickness—that for which the aggregates begin to merge and for which, as is well known, a rapid decrease in the electrical resistivity of the film occurs.

### (b) Rate of Evaporation

The effect of the rate of evaporation was studied by forming films in different times, viz.: 1.5, 8, 20, 30, and

† All micrographs shown are reversed in contrast, the metal appearing light on a dark background, and are at 75,000×.

<sup>13</sup> S. Tolansky, *Multiple-Beam Interferometry* (Clarendon Press, Oxford, 1948).

75 minutes and comparing their structure and properties which the "fast" films referred to in (a), which were formed in about 2 seconds. The more slowly evaporated silver films were in general more intensely colored. Micrographs showing the variation in structure with thickness for films formed in 20 minutes are given in Fig. 3a. It is clear that the "slow" films are generally more aggregated for thicknesses over 100Å. A comparison of the structure and thickness of the slow films of Fig. 3a with the fast films of Fig. 2a shows that the aggregates of slowly formed films tend to grow more in height, i.e., become thicker before joining together than do the aggregates of rapidly formed films which tend to remain thin and grow out over the substrate. For example the 175Å 20-min. film exhibits well-separated aggregates whereas the 180Å 2-sec. film is almost continuous. This effect is further illustrated in Fig. 4, in which a 580Å film formed in 20 minutes can be compared with a film of essentially the same thickness (560Å) formed in 75 minutes.

The optical transmissions and reflections are shown, against wave-length for a 20-min. evaporation in Fig. 3b, and against thickness for different rates at 6500Å in Fig. 3c. The effect of rate of evaporation on the optical properties is most strikingly indicated by the plot in Fig. 3d, of the absorption at 6500Å against thickness for different times. For slower rates the peak in the curve broadens and moves to greater thickness. The absorption of a 300Å film increases from about 2 percent at 2 sec. to 40 percent at 75 min. From work with other metals as well as silver this result appears to be quite general and suggests that for the optical metallic coatings usually required evaporations should be carried out as rapidly as possible. The practical importance of rate in such evaporations was apparently first noted by Crawford, Gray, Schawlow, and Kelly<sup>14</sup> of this laboratory, in the preparation of aluminium coated interferometer plates.

### (c) Temperature of Substrate

Temperature can have a marked effect on the structure of evaporated films. In the foregoing experiments the temperature of the substrate remained in all cases less than 35°C. However it was found that silver films formed on substrates at higher temperatures (70° to 300°C) showed greater aggregation and more pronounced colors, the changes increasing with tempera-



FIG. 7. Copper film 120Å thick (2-sec. evaporation).

<sup>14</sup> Crawford, Gray, Schawlow, and Kelly, *J. Opt. Soc. Am.* 39, 888 (1949).

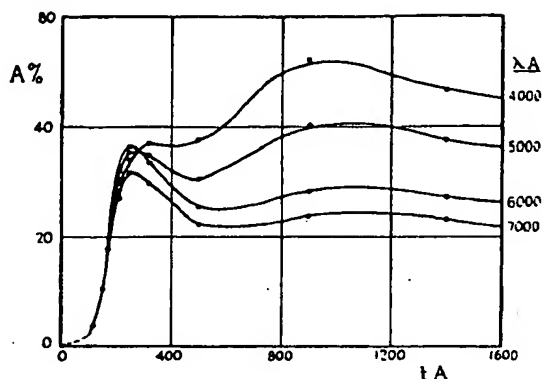


FIG. 8. The absorption of aluminum films against thickness.

ture. Heating normal "fast" films after formation produced films that were similar to those formed at the higher temperature.

#### (d) Other Metals

Rapidly evaporated (2-sec.) films of a number of other metals were studied to determine the dependence of optical characteristics on the properties of the metal.

##### (1) Gold

The structure resembled very closely that of the 2-sec. silver films. The thickness for which the aggregates began to merge was found to be approximately 180Å which is slightly greater than in the case of silver. Thinner films consisted of well-defined aggregates (see Fig. 5) while thicker films had a mottled appearance even when the substrate was completely covered.

The thinner gold films appear green and blue by transmitted light, red by reflected light. The variation in the transmission and reflection with thickness is rather similar to that of silver. The variation of the absorption with thickness (Fig. 6) shows a maximum for wave-lengths greater than 5000Å, but only a gradual increase with thickness for shorter wave-lengths.

##### (2) Copper

The structure was also aggregated in films thinner than 200Å (Fig. 7), but the aggregates did not appear as regular or as well-defined as in gold or silver films.

The light transmitted by copper films 200Å thick was of a green color which changed to blue at thicknesses below 50Å. The variation of the absorption coefficient with thickness was similar to gold but the maxima occur at slightly greater thicknesses and only for wave-lengths above 5500Å.

##### (3) Aluminum

Aluminum films had an aggregated structure at all thicknesses less than 300Å. The aggregates appeared to have poorly defined boundaries, but to maintain their individuality even in quite thick films.

Aluminum films showed little color effects by either transmitted or reflected light. The variation of the absorption with thickness (Fig. 8) gives maxima for all wave-lengths at a thickness of approximately 250Å, which are not as pronounced as in the case of silver particularly at the shorter wave-lengths. The maxima occurring at larger thicknesses (1000Å) correspond to minima in the reflection due to interference effects within the film.

##### (4) Antimony

In antimony films thinner than 400Å, well-defined regularly shaped aggregates were observed as shown in Fig. 9. The films appeared brown by transmitted light since the transmission was greater at all thicknesses for the longer wave-lengths. However, in contrast to the metals discussed above the absorption was found to increase continuously with increasing film thickness as shown in Fig. 10.

##### (5) Nickel

Films thinner than 300Å had an aggregated structure. Very small aggregates were observed in the thinner films (Fig. 11). The light transmission at thicknesses greater than 100Å was very nearly the same for all wave-lengths in the visible. With thinner films there was a slight maximum at 5000Å giving a green color to the films. Figure 10 shows the gradual increase in the absorption with increasing thickness.

##### (6) Palladium

Thin films appeared to have a fine aggregated structure although in general they were much more continuous than the films described above. The films showed very little color either by transmitted or reflected light. The absorption was found to be slightly greater at shorter wave-lengths but increased continuously with thickness (Fig. 10).

##### (7) Chromium

With the resolution obtainable in the electron microscope, chromium films even as thin as 20Å appeared continuous. The variation in the absorption with thickness showed only a gradual increase (Fig. 10) as in the case of antimony, nickel, and palladium films.

#### DISCUSSION

The migration of the metal after reaching the substrate is probably the most important factor in de-



FIG. 9. Antimony film 180Å thick.



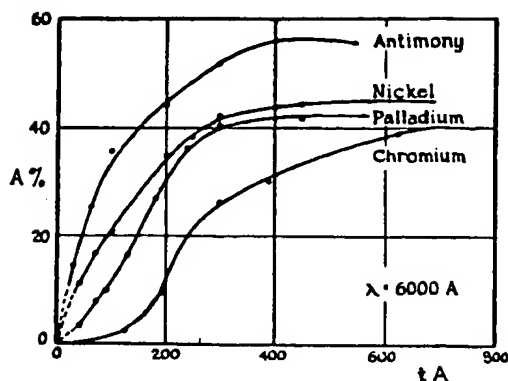


FIG. 10. Variation of the absorption of Sb, Ni, Pd, Cr. films with thickness (at 6000Å).

termining the stable form of thin metallic films. Some of the features of the process of migration have been discussed by Lennard-Jones<sup>17</sup> and by Appleyard.<sup>18</sup> It is clear that the migration will depend on the metal, the nature of the substrate, and the substrate temperature. The results on rates given indicate that the migration is a function also of the intensity of the incident stream of atoms, i.e. the number of atoms incident on unit area per unit time. It should be noted that in the experiments described here the intensity is not independent of film thickness, though the thicknesses studied varied by only a factor of 10 whereas the evaporation times were changed by a factor of over 2000. The manner in which the structure of the film depends on the rate of arrival of atoms at the substrate and their migration time and distance after reaching the substrate is not immediately evident. The experimental results however suggest that in the rapidly evaporated films the migration of an atom is altered by the subsequent arrival of other atoms in the same vicinity and presumably during what would be the normal or independent time of migration.

The brilliant colors observed in thin films of silver, gold, and copper cannot be explained by any of the ordinary principles of interference and diffraction. However, as has been described, they do depend on (1) the structure of the film since marked changes were produced by altering the rate of formation or the temperature either during or after formation, and on (2) the properties of the metal since films of different metals but with similar structure have quite different optical properties. Such results can be explained qualitatively from the theory of solids<sup>19</sup> by considering the absorption to be due to the free and bound electrons with the free electrons being more important for the longer wave-lengths and the bound electrons for the shorter wave-lengths. The transition between the two effects occurs in the ultraviolet for silver and aluminum,

in the visible for gold and copper, and in the infra-red for antimony, nickel, palladium, and chromium.

In the case of thick films the observed properties are very similar to those of the bulk metal. However marked differences occur in thinner films where the structure becomes aggregated. It may be assumed that for the aggregated films the absorption due to the free electrons will greatly increase. This was found in silver and aluminium films at all wave-lengths, and in gold and copper films for wave-lengths greater than 5500Å. However the absorption due to the bound electrons should show only a gradual change as was found in gold and copper films for wave-lengths shorter than 5500Å and in antimony, nickel, palladium, and chromium films for all radiations in the visible.

A classical theory developed by Garnett<sup>7</sup> can be used to explain some of the observed results in more detail. Using Rayleigh's calculation of the dipole induced in a metal sphere by a periodic electric field,<sup>20</sup> and Lorentz's result for the mutual influence of neighboring dipoles,<sup>21</sup> Garnett derived an expression for the effective refractive index  $n'$  and the effective extinction coefficient  $k'$  of a medium consisting of randomly distributed uniform metal spheres of radius much less than the wave-length of the exciting radiation. The calculation led to the following expressions for  $n'$  and  $k'$  in terms of  $n$  and  $k$ , the values for the bulk metal:

$$n'k' = \frac{3qb}{(1-qa)^2 + 4q^2b^2}, \quad (1)$$

$$k'^2 - n'^2 = 2 - \frac{3(1-qa)}{(1-qa)^2 + 4q^2b^2}, \quad (2)$$

where  $q$  is the volume of metal per unit volume of medium and necessarily  $0 < q < 1$ , and

$$a = \frac{(k^2 - n^2 + 1)(k^2 - n^2 - 2) + 4n^2k^2}{(k^2 - n^2 - 2)^2 + 4n^2k^2}, \quad (3)$$

$$b = \frac{3nk}{(k^2 - n^2 - 2)^2 + 4n^2k^2}. \quad (4)$$

Garnett then extended this theory to thin films in which case  $q$  depends on the structure and thickness of the film.

The product  $n'k'$  gives a measure of the absorption



FIG. 11. Nickel film 75Å thick.

<sup>17</sup> J. E. Lennard-Jones, *Trans. Faraday Soc.* 28, 333 (1932).

<sup>18</sup> E. T. S. Appleyard, *Proc. Phys. Soc. (London)* 49, 118 (1937).

<sup>19</sup> N. F. Mott and H. Jones, *The Theory of the Properties of Metals and Alloys* (Oxford University Press, New York, 1936).

<sup>20</sup> Lord Rayleigh, *Phil. Mag.* 44, 28 (1897).

<sup>21</sup> H. A. Lorentz, *Ann. d. Phys. und Chem.* 9, 641 (1880).



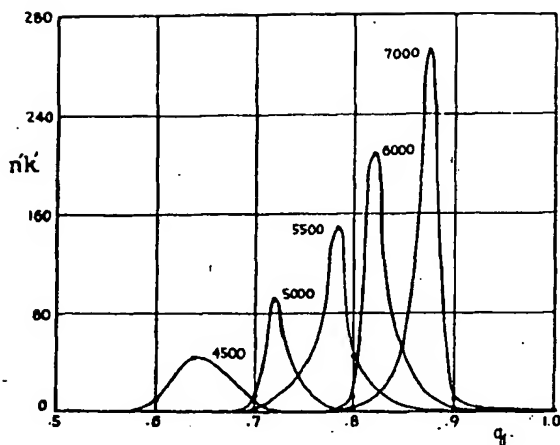


FIG. 12. The values of  $n'k'$  for silver films calculated from Garnett's theory.

of the film, the relationship derived by Goos<sup>22</sup> being:

$$n'k' = (\lambda/4\pi l)n_2(A/T), \quad (5)$$

where  $l$  is the thickness of the film,  $n_2$  is the refractive index of the substrate,  $\lambda$  is the wave-length of light,  $T$  is the transmission of the film, and  $A$  its absorption. Differentiation of (1) shows that  $n'k'$  and therefore the absorption will have a maximum if  $q^2 > 1/(a^2 + 4b^2)$ . Since  $q$  must be less than unity,  $a^2 + 4b^2 > 1$ . Substitution from (3) and (4) gives the condition that  $K > 0$ , where

$$K = 2(k^2 - n^2)^3 - 9(k^2 - n^2)^2 + (12 + 8n^2k^2)(k^2 - n^2) - 4 - 12n^2k^2. \quad (6)$$

The values of  $K$  calculated from the bulk constants<sup>23</sup> are given in Table I for the metals which were studied. This shows that for the cases where absorption maxima were observed, *viz.*, silver, gold, copper, and aluminum, the value of  $K$  is positive whereas in the other cases  $K$

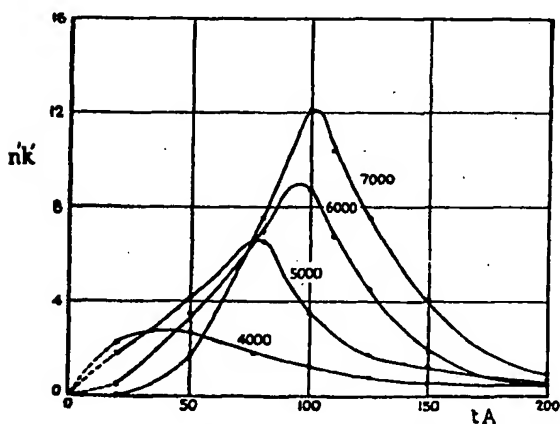


FIG. 13. The values of  $n'k'$  for silver films determined from the observed optical properties of the films.

<sup>22</sup> F. Goos, *Zeits. f. Physik* 100, 95 (1936).

<sup>23</sup> *International Critical Tables*, V, 248 (1929).

is negative. Assuming  $b$  to be small relative to  $a$ , as it usually is, the approximate condition for the presence of an absorption maximum is that  $k^2 - n^2 > 0.5$ , with the maximum in  $n'k'$  proportional to  $1/qb$  and occurring for  $q \approx 1/a$ .

In order to compare the above considerations with our results for the case of silver, the variation in  $n'k'$  with  $q$  was calculated from expression (1) and the plot is given in Fig. 12 for different wave-lengths. This shows that absorption maxima should occur, for successively shorter wave-lengths, at smaller values of  $q$  which correspond to decreasing thickness. The values of  $n'k'$  were also calculated from the observed absorption by expression (5) and are shown plotted in Fig. 13, against thickness. It is seen that the absorption maxima for silver vary with wave-length in the manner predicted by Garnett's theory, however they are smaller in value and broader. This may be explained by the fact that the films are composed of particles considerably different from the uniform spheres assumed in developing the theory.

TABLE I. Criterion for presence of a maximum in the variation of light absorption with thickness in thin metallic films:  $K > 0$  for maximum.

Metal	$\lambda$	$n$	$k$	$k^2 - n^2$	$K$
Silver	5890	0.18	20.6	425	$1.5 \times 10^4$
Gold	4000	1.58	1.13	-1.22	-107
	5800	0.42	6.65	44.3	$1.7 \times 10^4$
Copper	3950	1.17	1.50	0.88	-5.3
	6000	0.56	5.51	30.0	$5.2 \times 10^4$
Aluminium	5890	1.28	3.66	11.8	$2.0 \times 10^3$
Antimony	5890	3.04	1.63	-6.6	$-2.6 \times 10^3$
Nickel	5890	1.79	1.86	0.25	-35
Palladium	6000	1.92	1.31	-1.9	-270
Chromium	6080	3.28	1.31	-9.7	$-4.4 \times 10^3$

Similar calculations for gold films show that absorption maxima are predicted by the theory only for wave-lengths greater than 5000A, as indeed was found.

When the films were prepared at a slower rate or heated during or after formation, they were found to be more aggregated which corresponds to a decrease in the value of  $q$ . For such changes the theory predicts that the absorption maxima should occur at shorter wave-lengths for the same thickness, or at greater thicknesses for the same wave-lengths. The latter case is illustrated in Fig. 3d.

Garnett's theory can also be used to explain observations on metals other than those studied here; for example, the absorption maxima found by Wood<sup>24</sup> in films of sodium and potassium which had an aggregated structure visible in the light microscope. Fukuroi<sup>25</sup> reported similar maxima in mercury, cadmium, and zinc films prepared and studied at low temperatures. As can be predicted from Garnett's theory, for each of these three metals the magnitude of the maxima in the

<sup>24</sup> R. W. Wood, *Phil. Mag.* 38, 98 (1919).

<sup>25</sup> T. Fukuroi, *Inst. Phys. and Chem. Research Tokyo* 32, 172 (1937).

absorption varied with wave-length in the opposite sense to the variation for silver, gold, and copper.

### CONCLUSIONS

Evaporated metallic films when sufficiently thin are in general aggregated in structure. The aggregation depends not only on the metal, the substrate, and the temperature, but also on the rate of deposition of the film.

In the region of thickness for which marked changes of light absorption occur, the aggregates are beginning to merge to form a more nearly continuous film.

Garnett's classical theory of the optical properties of thin metallic films which is expressed in terms of the structure of the films and the optical constants of the

bulk metal predicts, in a qualitative way, all the observed results.

As rapid rates of formation reduce aggregation for a given thickness, and this in turn reduces the light absorption, one of the conditions for the production of high quality reflection coatings is a high rate of deposition of the metal.

### ACKNOWLEDGMENTS

We wish to express thanks to Professor M. F. Crawford for stimulating the investigation of the evaporation rate, to Mr. T. A. McLauchlan for assistance in some of the experimental work, and to Mr. D. R. Welch for reproduction of the micrographs.

## Dark Adaptation Level and Size of Testfield

ERNST WOLF AND MICHAEL J. ZIGLER

*Psychological Laboratory and Visual Research Laboratory,\* Wellesley College, Wellesley, Massachusetts*

(Received December 14, 1949)

Data for dark adaptation curves were obtained for four square fields, subtending respectively 2.5, 5, 10, and 20 degrees at the eye, (a) when the subject indicated when light could just be perceived and (b) when parallel fine lines could just be detected. The levels attained in both the cone and in the rod segments of this function were found to vary when the area of the testfield exposed to the eye was changed, being higher for a smaller than for a larger testfield. This denotes that sensitivity is greater for a larger than for a smaller field of retinal stimulation. These findings indicate that the limit between so called photopic and scotopic vision is not to be regarded as fixed and definite but as functionally variable.

THE retinal cones are usually regarded as the receptive elements involved in photopic vision, and the rods basic to scotopic vision. The nature of the dynamic changes occasioned in each of the two kinds of retinal receptor during photic stimulation has recently been intensively investigated. First to be identified was a reversible cycle of changes occurring in the rods—rhodopsin $\rightleftharpoons$ retinene $\rightleftharpoons$ vitamin A, and later a similar cycle for the cones involving iodopsin has been detected.<sup>1</sup>

One approach to the study of the functional interrelationship existing between photopic and scotopic vision conceivably may be made in terms of a careful study of the dark adaptation function. This function is based on sensitivity measurements made at intervals during a stay in the dark. The nature of the general characteristics of the function has been under special study for some years.<sup>2,3</sup>

If the eye has been just previously exposed to a bright field, the dark adaptation function obtained is known to be duplex in form, i.e., made up of two segments; the first supposedly is based on cone vision, and the second on rod vision. During the first few minutes in the dark, sensitivity to light increases very rapidly, then more slowly until the function is asymptotic with respect to the abscissa. Sensitivity to light begins suddenly to increase again, rapidly at first, then progressively more and more slowly, gradually approaching a constant value. The total extent of the descent in the first (cone) segment of the dark adaptation function for specific experimental conditions has been estimated to represent an increase in sensitivity of about one hundred fold, while that of the second (rod) segment comprises a much greater increase in sensitivity, perhaps one hundred times that represented in the descent of the cone segment.<sup>4,5</sup>

Experiments have indicated that the dark adaptation function does not maintain the same level when the size of the testfield used in measuring sensitivity thresholds

\* Sponsored by American Optical Company.

<sup>1</sup> G. Wald, *Vision: Photochemistry. Medical Physics* (Year Book Publishers, Chicago, 1944).

<sup>2</sup> A. Kohlrausch, *Handbuch d. normalen und pathologischen Physiol.* 12, 1499 (1931).

<sup>3</sup> H. Piper, *Zeits. f. Psych. und Physiol. d. Sinnesorgane*. 31, 161 (1903).

<sup>4</sup> S. Hecht, "Vision II," *Handbook Gen. Exp. Psychol.* (Clark University Press, Worcester, Mass., 1934).

<sup>5</sup> Hecht, Haig, and Wald, *J. Gen. Physiol.* 19, 321 (1935).